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Properties of humic acids of Arctic tundra soils in Spitsbergen

ABSTRACT: On the basis of elemental composition, optical properties in the visible region, infrared spectra and thermal analysis (TG, DTG, DTA), humic acids of tundra soils in Spitsbergen are found to be more similar to fulvic acids than to humic acids of soils from other soil-climatic zones. The authors claim that it results from climatic conditions (low temperature, considerable humidity, alternation of freezing and thawing) and specific biochemical composition of tundra plants (predominance of plants devoid of lignin) which constitute substratum of the studied humic acids.

Key words: Arctic, Spitsbergen, soil, soil humus, humic acids.

Introduction

Transformation of organic remains in the Arctic tundra soils proceeds under specific conditions which are exclusively characteristic for this bioclimatic-soil zone. Low temperature and considerable humidity as well as a short period of biological activity (2—3 months a year) are not favourable for mineralization and humification (Douglas and Tedrow 1959, Dergačeva 1984, Dziadowiec 1983, 1992; Fiszer and Bieńkowski 1987, Fiszer 1990, Ross 1989). Therefore, soils of a polar zone contain much organic matter, notwithstanding a limited input of organic remains determined by a low primary production (Plichta 1993). Tundra plant associations are dominated over by plants completely devoid of lignin or those containing a little amount of it (algae, mosses, lichens

— Gugnacka-Fiedor and Noryskiewicz 1982, Plichta and Luścińska 1988). This fact must affect a course of humification and properties of its products, because lignin plays a crucial role in formation of humus compounds (Flaig 1964, Kononowa 1968, Stevenson 1982, 1985). Climatic conditions in the Arctic tundra affect also the properties of soil humus compounds (Dergačeva 1984, Ross 1989). Alternation of freezing and thawing can cause breakup of humus molecules.

It has been assumed therefore that humic acids (HA) formed in such specific conditions are essentially different from HA originating in other bioclimatic-soil zones. The aim of the paper is to verify this hypothesis.

Materials

Humic acids were extracted from soils of the seaside plain Kaffiöyra (northwestern Spitsbergen: 78°40'N, 11°40'E), which excels itself in marine polar climate. The average annual temperature at the Isfiord Radio Station some 70 km to the southeast from Kaffiöyra is -4.7°C , and the average annual rainfall is 435 mm (Steffensen 1982). Kaffiöyra indicates a large diversity of a soil cover, resulting from variety of parent material (mainly marine sands and gravels, loams of different origin, as well as contemporary glaciofluvial deposits) and water conditions (Plichta 1993).

Organic (O) and humic horizons (A) of Gelic Regosols, Gelic Cambisols and Gelic Gleysols (FAO 1989) were examined. Some samples were also taken from organic horizons of tundra hummocks — characteristic for tundra microrelief (Plichta 1993). Properties of the analyzed soil samples are presented (Table 1).

Table 1

Some properties of tundra soils in Spitsbergen.

Soil	Soil horizon	Depth [cm]	HA No	TOC	TN	C/N	pH	CHA	CHF	C—CH
				[% of d.w.]				[% of TOC]		C—FA
Gelic Regosol	(O) A	0.5—0 0—1	1 2	4.09 1.64	0.308 0.091	13.3 18.0	7.2 7.7	7.09 3.05	28.12 13.41	0.25 0.23
Gelic Cambisol	O O+A	3—0 0—6	3 4	5.19 7.16	0.371 0.769	14.0 9.3	6.9 6.4	23.89 34.50	34.68 41.76	0.44 0.83
Gelic Gleysols	O O A O	3—0 1—0 0—9 1—0	5 6 7 8	13.97 9.22 3.93 5.50	1.213 0.478 0.279 0.459	11.5 19.3 14.1 12.0	6.9 6.5 6.8 7.2	29.56 17.68 31.55 26.18	22.91 28.09 34.61 21.45	1.29 0.63 0.91 1.22
Tundra hummocks	Ol Ofh	4—2 2—0	9 10	15.29 5.43	1.056 0.468	14.5 11.6	4.0 4.0	27.99 35.91	30.54 46.22	0.92 0.78

TOC — total organic carbon content, TN — total nitrogen content, dw — dry weight, CHA — carbon of humic acids, CFA — carbon of fulvic acids

Methods

Humic acids (HA) were extracted from soil samples according to the Schnitzer's method (Schnitzer and Skinner 1968, Griffith and Schnitzer 1975). The following analyses were performed:

- elemental composition with a use of the CHN-240 Perkin-Elmer microanalyser, oxygen and sulphur were calculated by difference;
- optical properties in visible region for 0.02% solutions of HA in 0.05 M of NaHCO₃ (Chen et al. 1977): absorbance curves, coefficients $E_{4/6}$ (ratio of absorbances at $\lambda = 465$ nm and $\lambda = 665$ nm) and $E^{0.001}$ values (absorbance of 0.001% solutions of HA at $\lambda = 465$ nm), recommended by Orlov (1990) as characteristic for HA of various soil types;
- infrared spectra on KBr disc (3 mg HA dry sample + 800 mg KBr) on a Specord 75IR (Carl Zeiss Jena);
- thermal analysis on the derivatograph OD 102 (Paulik-Paulik-Erdey system), under the following conditions: 40 mg of HA mixed with Al₂O₃ in the ratio 1:9, ΔT 3.3°C min⁻¹, heating up to 600°C in the air.

The energetic value of humic acids has been calculated on the basis of the formula:

$$Q = k.S.m^{-1}$$

where Q — calorific value of HA in KJ.g⁻¹, k — proportional coefficient determined experimentally on the basis of thermal analysis of the Merck's HA, S — surface below the DTA curve (cm²), m — weight of HA (g), oxidation of which caused the exothermic effect with the surface S .

Results and discussion

Elemental composition

Elemental composition of humic acids of tundra soils in Spitsbergen differs evidently from elemental composition of HA of soils of a temperature climatic zone and from soils of other regions in the Arctic. Comparison of the data (Tables 2 and 3) reveals that the studied acids contain relatively small amount of carbon and large amounts of hydrogen and oxygen. Their elemental composition is much similar to the fulvic acids than to the humic ones. Those differences are the most apparent on the atomic H:C versus O:C diagram (Fig. 1). High H:C values prove low aromatization of the studied humic acids (Kononowa 1969, Orlov 1990).

The oxidation degree of the tundra soil humic acids (ω — Table 2) is positive, which proves considerable oxidation of their molecules. Similar values of ω for HA of agricultural soils in Poland were established by Gonet (1989). On the other hand, the humic acids from forest soils in Poland are more reduced, as most of their oxidation coefficients are negative (Dziadowiec 1979).

T a b l e 2

Elemental composition of humic acids of tundra soils in Spitsbergen, their oxidation degree (ω) and optical properties.

No of HA	C H N O+S				H/C	O/C	ω	$E^{0.001}$	$E_{4/6}$
	[% of dry ash-free basis]								
1	47.67	6.26	6.51	39.56	1.58	0.62	0.02	0.0086	5.39
	30.17	47.53	3.53	18.77					
2	44.89	5.54	3.77	45.80	1.48	0.77	0.27	0.0231	5.89
	30.14	44.63	2.17	23.06					
3	48.65	5.49	4.15	41.71	1.35	0.64	0.15	0.0190	6.98
	32.57	44.11	2.38	20.94					
4	43.79	5.14	3.97	47.10	1.41	0.81	0.44	0.0208	6.07
	30.37	42.77	2.36	24.50					
5	47.11	5.46	5.30	42.13	1.39	0.67	0.24	0.0175	6.90
	31.66	44.04	3.06	21.24					
6	47.45	5.48	4.68	42.39	1.38	0.67	0.21	0.0208	7.74
	31.84	44.14	2.69	21.33					
7	47.21	5.46	3.90	43.43	1.39	0.69	0.20	0.0170	6.18
	31.76	44.08	2.25	21.91					
8	46.10	5.57	4.75	43.58	1.45	0.71	0.23	0.0174	6.27
	30.80	44.65	2.72	21.83					
9	48.11	5.40	4.00	42.49	1.37	0.66	0.19	0.0165	7.49
	32.46	43.72	2.32	21.50					
10	46.63	5.48	3.60	44.29	1.41	0.71	0.21	0.0249	7.07
	31.36	44.23	2.07	22.34					

Numerator — in weight %, denominator — in atomic %

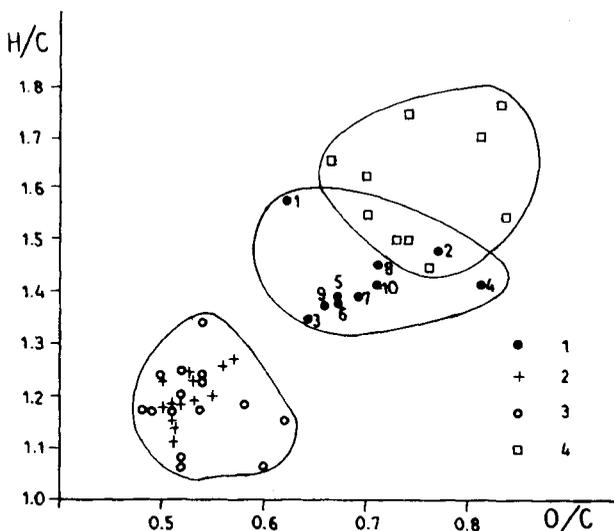


Fig. 1. Atomic H/C versus O/C diagrams

1 — humic acids of tundra soils in Spitsbergen, 2 — humic acids of cultivated soils in Poland (Gonet 1989), 3 — humic acids of forest soils in Poland (Dziadowiec 1979), 4 — fulvic acids of forest soils in Poland (Dziadowiec 1979).

Elemental composition of humic and fulvic acids (literature data).

Table 3

Origin of HA	C	H	N	O+S	Author
	[% of dry ash free basis]				
Humic acids					
USSR cultivated and forest soils	52—62	3.0—5.5	3.5—5.0	30—33	Kononowa (1968)
Polish cultivated soils	51—57	3.8—5.5	3.4—5.9	34—40	Gonet (1989)
Polish forest soils	53—57	4.9—5.9	1.2—4.6	36—38	Dziadowiec (1979)
Arctic soil	56.2	6.2	4.3	32.8	Schnitzer and Khan (1978)
Fulvic acids					
USSR cultivated and forest soils	44—49	3.5—5.0	2.0—4.0	44—49	Kononowa (1968)
Polish forest soils	44—48	5.6—7.5	0.3—1.7	44—48	Dziadowiec (1979)
Arctic soil	47.7	5.4	1.1	44.2	Schnitzer and Khan (1978)

Optical properties in visible region

The humic acids of tundra soils in Spitsbergen present a relatively low absorbance in the visible region. All the absorbance curves have a steadily falling course, with a little inflection at $\lambda = 550$ nm. $E^{0.001}$ values vary from 0.0086 to 0.0249 (average 0.0187), and the coefficient $E_{4/6}$ varies from 5.39 to 7.74 (average 6.60) (Table 2).

According to Orlov (1990), the average value of $E^{0.001}$ for HA extracted from different tundra soils equals to 0.029, and for humic and fulvic acids of soils from other soil-climatic zones equals to 0.049—0.113 and 0.010—0.017, respectively. Therefore, the absorbance $E^{0.001}$ of the studied humic acids in its upper limit approaches the values, characteristic according to Orlov (1990) for HA of tundra soils, and in its lower limit the values for fulvic acids.

Values of the coefficient $E_{4/6}$ indicate also a higher similarity of the studied HA to the fulvic acids rather than to the humic ones. According to Kononowa (1968), values $E_{4/6}$ for humic acids of Podzols and Nitosols equal approximately to 5.0, for humic acids of Chernozems to 3.0—3.5, and they assume intermediate values for humic acids of other soils. On the other hand, the fulvic acids are characterized by $E_{4/6}$ from 6.0 to 8.5. Similar values of this coefficient for humic and fulvic acids are given by Chen *et al.* (1977), Stevenson (1982) and Orlov (1990). Thus only the lowest values of the optical density coefficient of HA of soils in Spitsbergen approach the coefficients for HA of soils in other zones.

Therefore, optical properties of the humic acids of soils in Spitsbergen are more similar to those of the fulvic than of the humic acids. Since values of the coefficient $E_{4/6}$ are inversely proportional to the average molecular weight of humic compounds (Kononowa 1968, Stevenson 1982, Orlov 1990), high values

of this coefficient suggest that molecules of the humic acids of soils in Spitsbergen are characterized by relatively low molecular weights.

Infrared spectra

In infrared spectra of the tested humic acids there are all absorption bands, characteristic for this group of organic compounds (Fig. 2). Comparing IR spectra of HA extracted from different soils in Spitsbergen, infrared spectra of HA Gelic Regosols have been found to indicate a specific course and sharpness of absorption bands. In the region of $2800\text{--}3000\text{ cm}^{-1}$ distinct separation of 2920 and 2960 cm^{-1} bands was observed, absent in spectra of HA samples extracted from other soils in Spitsbergen. The analyzed bands indicate that in HA molecules of Gelic Regosols there are methyl and methylene groups, connected both with aromatic rings and aliphatic chains.

In other region of IR spectra for all the studied HA, similar absorption bands are observed, however they are different in their intensity. Characteristic absorption bands of $1710\text{--}1720$ and $1620\text{--}1660\text{ cm}^{-1}$ indicate presence of carboxyl groups in acids and ketons (the first of them) as well as of —C=O and =NH groups in amides, and C=C in aromatic rings (the second one). Absorption bands determined by presence of amide II band and aromatic

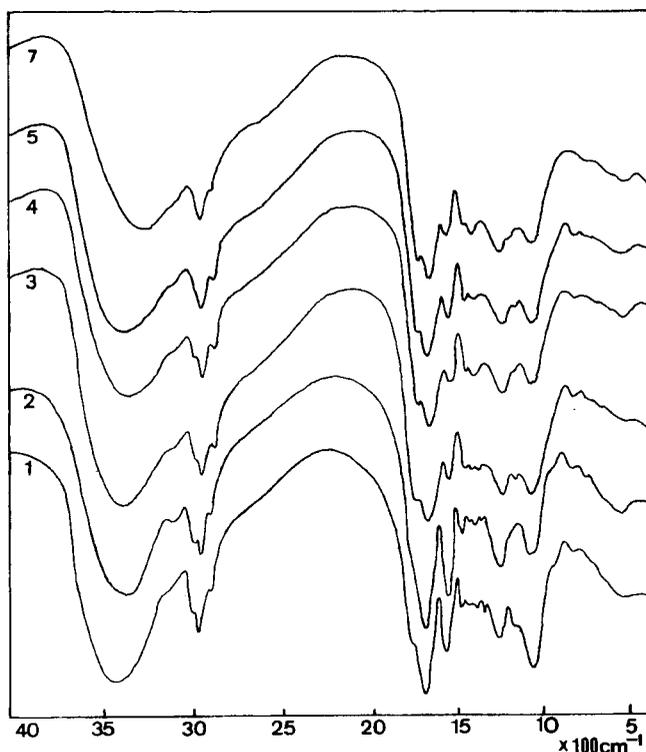


Fig. 2. Infra-red spectra of humic acids.

structures in HA occur in the region of 1540 and 1510 cm^{-1} respectively. Spectra of HA (particularly of Gelic Regosols) display absorption bands in the region 1460 cm^{-1} ($-\text{CH}_3$ and $=\text{CH}_2$ groups in alkanes and cycloalkanes). In all the spectra of humic acids from tundra soils, two broad absorption bands has been detected: at approximately 1200 and 1000 cm^{-1} (alcoholic $-\text{OH}$ groups, $-\text{OCH}_3$, and polysaccharides) (Drozd 1978, Gonet 1989, Orlov 1990). In this region of spectra, bands caused by presence of clay minerals may occur, but such possibility is excluded by low ash content of the tested HA as well as by absence of other absorption bands characteristic for clay minerals. The absorption intensity in the region from 1000 to 1100 cm^{-1} is usually higher in the spectra of HA, extracted from organic horizons of soils. It particularly concerns the Gelic Regosols.

A comparative analysis of the IR spectra indicates that humic acids of Gelic Regosols differ in their properties from humic acids of other soils and their structure is much similar to the one of fulvic acids. Spectra of HA from other tundra soils are similar to spectra of humic acids from Podzols of a temperate climatic zone. Nevertheless, it should be kept in mind that analysis of IR spectra (in particular minimal differences between them) requires to take into consideration polydispersive and polymolecular character of humic acids, what makes precise interpretation of spectra difficult.

Thermal analysis

Thermal decomposition of studied humic acids occurs in an endothermal and two or three exothermal reactions (Table 4, Fig. 3). Maximum of the endothermal reaction occurs at temperature of 70–80°C and accompanying loss weight of the HA, which varies from 6 to 8% (Table 4).

Table 4

Parameters of thermal decomposition of humic acids of tundra soils in Spitsbergen.

No. of HA	Maximum temperature of effects on DTA curve [°C]				Loss of weight corresponding with effects on DTA curve [%]				$\frac{6+7}{8+9} = Z$
	endo	exo ₁	exo ₂	exo ₃	endo	exo ₁	exo ₂	exo ₃	
1	2	3	4	5	6	7	8	9	10
1					not determined				
2	75	300	410	485	10.71	46.32	37.59	5.38	1.33
3	75	307	410	490*	6.62	45.26	48.12	—	1.08
4	75	290	375	460	15.19	44.30	25.32	15.19	1.47
5	80	310	420	505	7.14	55.20	24.67	12.99	1.66
6	80	312	415	470*	5.63	51.25	43.12	—	1.32
7	80	300	395	lack	8.13	51.25	40.62	—	1.46
8	75	310	420	470*	6.88	55.62	37.50	—	1.67
9	80	310	410	480	7.79	51.30	27.27	13.64	1.44
10	70	300	390	450*	7.50	52.50	40.00	—	1.50

Z — „aliphaticity” degree of HA, * third exothermal reaction as inflection

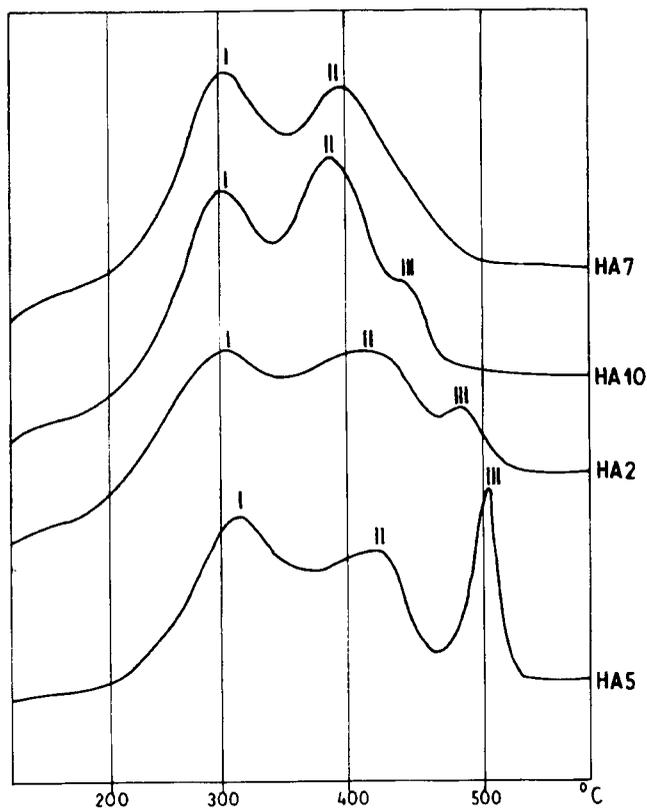


Fig. 3. DTA curves of humic acids.

The maximum of the first exothermal reaction was observed at temperature of 290—350°C. As result of this reaction, 44—48% of weight of the HA in Gelic Regosols and Gelic Cambisols as well as 51—56% in Gelic Gleysols and tundra hummocks are oxidated (Table 4, Fig. 3).

The second exothermal reaction occurs at temperature of 390—420°C *i.e.* about 100° higher than the previous one. Weight loss due to this reaction was equal to 37—48% of HA, decomposition of which occurs in two exothermal reactions (HA 3, 7, 8 and 10), and 24—36% of the HA with a third, distinctly separate exothermal reaction. The latter is clearly recognizable only in four samples (HA 2, 4, 5 and 9) and in the other four ones, it forms an inflexion (HA 3, 6, 8 and 10). This reaction reaches its maximum at temperature of 480—505°C, and weight loss connected with this reaction varies from 5 to 26%.

Humic acids of tundra soils in Spitsbergen are characterized by predominance of substance which reacts at low temperature (endothermal reaction and the first exothermal reaction), however some of this substance in HA of Gelic

Regosols and most Gelic Cambisols is smaller than in HA of Gelic Gleysols and tundra hummocks.

On the basis of thermal analysis of humus compounds from forest and cultivated soils in Poland a number of reactions in thermal destruction on those compounds, as well as amount of substance reacting in particular reactions are confirmed to have been connected with "maturity" and molecular structure of humic acids (Dziadowiec 1979, Gonet 1989). In a low-temperature mainly aliphatic structures whereas in high-temperature mainly aromatic structures of humic acids molecules are decomposed. The ratio of weight loss in low and high temperatures (coefficient *Z* in Table 4) proves the aliphaticity of molecules of humic acids. The higher the coefficient *Z*, the higher is a portion of aliphatic structures in HA molecules and *vice versa*.

Assuming this interpretation, in molecules of the studied humic acids the aliphatic structures are found to be predominant. Humic acids of Gelic Regosols and Gelic Cambisols are characterized by higher aromatization degree of their molecules than humic acids of Gelic Gleysols and those of tundra hummocks. The third exothermal peak was connected by Gonet (1989) with presence of separate aromatic structures, formed directly from incompletely transformed precursors of humic acids.

Calorific values of humic acids of soils in Spitsbergen vary from 17 to 20 kJ.g⁻¹ (Table 5). Aliphatic and aromatic parts of HA molecules differ with regard to energetic properties. The calorific value of aliphatic structures varies from 15 to 22 kJ.g⁻¹, and of aromatic ones — from 20 to 29 kJ.g⁻¹ (Table 5). The highest calorific values are typical for the structure, oxidation of which is connected with the third exothermal reaction.

T a b l e 5

Energetic parameters of thermal decomposition of humic acids of tundra soils in Spitsbergen.

No. of HA samples	Calorific value kJ.g ⁻¹			
	total	exo ₁ *	exo ₂ *	exo ₃ *
1		not determined		
2	19.32	17.38	19.79	34.22
3	18.98	18.15	22.01	—
4	22.48	21.60	23.47	23.36
5	16.85	14.57	22.99	26.41
6	20.29	18.44	25.13	—
7	18.50	18.28	22.46	—
8	19.07	18.02	24.12	—
9	19.81	17.33	26.69	26.69
10	20.37	16.92	28.72	—

* for substance combusted during exothermal reaction

Results of the thermal analysis confirmed that humic acids of tundra soils in Spitsbergen indicate many features, typical for "young" humic acids, namely:

- considerable portion of aliphatic structures in HA molecules, what is proved by high values of the coefficient Z ,
- relatively low calorific values,
- presence in some HA samples of a third exothermal reaction, absent in "mature" humic acids.

Conclusions

Humic acids of tundra soils in Spitsbergen have many properties characteristic for "young" humic acids and they are similar to the fulvic acids rather than to the humic ones from the other soil-climatic zones. It seems that this is a relative feature, independent from a real age but caused by rate of processes, which proceed under such severe climatic conditions as well as by biochemical composition of initial plant material. Specific composition of tundra plants may result in a lower "aromaticity" of the tested humic acids.

Molecules of humic acids of tundra soils in Spitsbergen are characterized by a relatively low molecular weight. It is possible that this phenomenon results from alternation of freezing and thawing which can cause disruption of molecules of the humic acids.

Infrared spectra and results of thermal analyses of HA of soils which belong to different soil types, display certain peculiarity which indicates differences in molecular structure of humic acids. The latter seems to depend on different course of humification.

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Streszczenie

Kwasy huminowe wyekstrahowano z poziomów organicznych (O) i próchnicznych (A) gleb tundry arktycznej Spitsbergenu (tab. 1). Na podstawie składu pierwiastkowego (tab. 2-3, fig. 1), właściwości optycznych w świetle widzialnym (tab. 2), widm w podczerwieni (fig. 2) stwierdzono, że KH z gleb arktycznych wykazują wiele cech charakterystycznych dla „młodych” kwasów huminowych i często bardziej przypominają kwasy fulwowe niż kwasy huminowe. Molekuły badanych KH w porównaniu z KH gleb innych stref bioklimatyczno-glebowych zawierają mniej węgla, a więcej wodoru i tlenu (fig. 1). Wykazują także mniejszy stopień aromatyzacji, stosunkowo niskie masy cząsteczkowe. Wnioski te potwierdzają rezultaty analiz derywatograficznych TG, DTG, DTA (tab. 4-5, fig. 3). Autorzy uważają, że jest to rezultat powolnego tempa procesów humifikacji i specyficznego składu biochemicznego roślin tundrowych (dominacja roślin pozbawionych ligniny) stanowiących substrat badanych kwasów huminowych. Na wielkość cząsteczek mogą mieć również wpływ procesy przemiennego zamarzania i rozmarzania powodując rozrywanie molekuł humusowych.